Consommation et Affaires commerciales Canada
Consumer and Corporate Affairs Canada

Bureau des brevets
Patent Office

Ottawa, Canada
K1A 0C9

(21) (A1) 2,104,846

(22) 1993/08/25

(43) 1994/03/03

5,071,3/93

(51) INTL.CL.[5] C09D-017/0

(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Pigment Pastes, Process for Producing Pigment Pastes and the Use Thereof for the Pigmentation of Coating Agents

(72) Bajorat, Gerda - Germany (Federal Republic of) ;
Hamel, Claudia - Germany (Federal Republic of) ;
Kern, Hartmut - Germany (Federal Republic of) ;

(71) Same as inventor

(30) (DE) P 42 29 196.8 1992/09/02

(57) 10 Claims

Herberts GmbH

Abstract:

Pigment pastes are produced by pasting or blending one or several pigments and/or fillers in a paste resin based on a polyester oligomer polyacrylate which is obtainable by radical polymerisation of

A) 80 - 50 wt% of

a) one or several hydroxyfunctional acrylic acid esters and/or methacrylic acid esters and
b) one or several monofunctional ethylenically unsaturated acids, as well as, optionally,
c) one or several alpha,beta-ethylenically unsaturated monomers without functional groups in

B) 20 - 50 wt% of one or several hydroxyfunctional polyester oligomers with a calculated molecular weight of 200 - 1000, a hydroxy number of 280 - 600 and an acid number of 0 - 1.5, obtainable by polycondensation of one or several diols, polyols and dicarboxylic acids and derivatives thereof,

whereby the monomers a), b) and c) are used in such quantities as to ensure that the polyester oligomer polyacrylate obtained has a hydroxyl number of 150 - 390 and an acid number of 16 - 40. The pigment pastes are suitable for the pigmentation of the most diverse coating agents, both water-based and non-aqueous.

Also described are the pigment pastes obtained and the use thereof in the production of coating agents and lacquer coatings.

Herberts GmbH

Pigment pastes, process for producing pigment pastes and the use thereof for the pigmentation of coating agents

The invention relates to the provision of a pigment paste having wide applicability and which is suitable in particular for the production of pigmented basecoat and topcoat lacquers.

Since the introduction of water-dilutable basecoat and topcoat lacquers the problem arises for lacquer manufacturers of having to produce and stockpile every colour tone in the form of the water-dilutable lacquer and also of the solvent-based lacquer or the relevant initial products, so as to be able to conform to the different equipment available to the users. In the case of automobile lacquers, for example, the automobile assembly-line lacquer of the same colour tone and the automobile repair lacquer, optionally in several variants as regards the drying mechanism, have to be available.

In respect of each lacquer system it is necessary to make use of a special pasting component for the production of a suitable pigment paste. After production of the pigment paste the formulation of the lacquer is completed with, in each case, one or several additional binding agents. In this regard the constituents must be coordinated with one another so as to obtain a suitable coating agent - eg, the coating agent has to be stable in storage and satisfy the demanding optical requirements. In this connection it is possible to effect pasting within the main binding agent of the lacquer, or special paste resins (pasting resins) are used with a view to production of the pigment paste.

A general problem now consists in the need to make available and stockpile a pigment paste for each colour tone in respect

of each different lacquer system. As a result, manufacture becomes costly and considerable storekeeping becomes necessary.

Particular problems arise in the case of the production and storage of water-dilutable lacquer systems or the water-dilutable pigment pastes on which they are based. In this case use can only be made of corrosion-resistant production plants and barrels, made of high-quality alloy steel, for example, and the temperatures prevailing at the storage depot must be such as to prevent freezing, since this may result in the aqueous lacquer materials being damaged.

In EP-A-0 052 224 pigment pastes are described which serve to produce aqueous or solvent-containing lacquers. They consist of binding agents with a high solvent content based on copolymers of water-soluble N-vinyl compounds. However, lacquers produced with such pastes exhibit high sensitivity to water.

In DE-A 39 10 829 aqueous coating agents are described which are produced on the basis of water-soluble polyester oligomer polyacrylates, which have been neutralised with bases, together with crosslinking agents. These coating agents are particularly suitable for use as clear-lacquer coating agents. The binding agents are used as an aqueous solution.

The object of the invention is the provision of a pigment paste which can be used in various lacquer systems, for example in aqueous and non-aqueous lacquer systems, by means of which the disadvantages stated above, such as high development cost, a considerable storage requirement, small deposit sizes and instability when exposed to frost, are avoided.

It has been shown that this task can be achieved by the provision of a process for producing a pigment paste by

pasting or blending one or several pigments and/or fillers in a paste resin (pasting resin), said process being characterised in that use is made by way of paste resin of a polyester oligomer polyacrylate which is obtainable by radical polymerisation of

A) 80 - 50 wt% of

a) one or several hydroxyfunctional (meth)acrylic acid esters (the term (meth)acrylic used here should be taken to mean acrylic and/or methacrylic) and

b) one or several monofunctional ethylenically unsaturated acids

and, optionally,

c) one or several alpha,beta-ethylenically unsaturated monomers differing from a) and b) and without functional groups, in

B) 20 - 50 wt% of one or several polyester oligomers with a calculated molecular weight of 200 - 1000, preferably 300 - 600, an OH-number of 280 - 600, preferably 400 - 500 mg KOH/g, and an acid number of 0 - 1.5 mg KOH/g, obtainable by polycondensation of one or several diols, polyols and dicarboxylic acids and derivatives thereof,

whereby the monomers a), b) and c) are used in such quantities as to ensure that the polyester oligomer polyacrylate obtained has a hydroxyl number of 150 - 390 mg KOH/g and an acid number of 16 - 40, preferably 20 - 30 mg KOH/g.

The invention also relates to pigment pastes which have been produced as described above and which exhibit a ratio of pigment or filler to paste resin, in each case relative to the weight of solids, of 0.05 to 2.5 : 1.

In the production of the polyester oligomer polyacrylate which is used in accordance with the invention the polyester oligomer component B) is submitted and the monomer component A) is polymerised therein. Polyester oligomer polyacrylates

of this type are described in DE-A-39 10 829 by way of binding agent for aqueous coating agents.

The calculated molecular weight M is determined in accordance with T.C. Patton, Alkyd Resin Technology, "Formulating Techniques and Allied Calculations", 1962, page 106 ff, as follows

$$M = \frac{W}{(M_o - e_a) + \frac{W_{(AN)}}{56100}}$$

M = average molecular weight calculated
W = weight of all components less condensation water
M_o = number of all moles
e_a = equivalents of the acid
$W_{(AN)}$ = acid number of the polyester oligomer

The polyester oligomer can be used for production of the polyester oligomer polyacrylate without solvent as sole reaction medium.

In the production of the polyester oligomer polyacrylate, however, it is also possible to add a solvent for the polyester oligomer. Any typical lacquering solvent may be used.

Suitable solvents are preferably those which are miscible with water to an unlimited extent - eg, monovalent aliphatic alcohols such as those having 2 to 4 carbon atoms, eg, ethanol and isopropanol, or ketones, eg, acetone or methyl ethyl ketone, or glycol ethers such as methyl glycol, ethyl glycol, butoxyethanol, methoxypropanol, ethoxypropanol and methoxypropoxypropanol, or diols such as ethylene glycol and propylene glycol, or polyether diols such as polyethylene

glycol and polypropylene glycol, or any other solvents pertaining to other classes of compound, said solvents being miscible with water to an unlimited extent, or of mixtures of the aforementioned compounds or classes of compounds. But use may optionally also be made, in part only, of those solvents which are only miscible with water to a limited extent or not miscible with water at all. The organic solutions of the polyester oligomer acrylates possess a solvent content of up to 30 wt%, preferably below 20 wt%.

The polyester oligomer used as reaction medium in the production of the polyester oligomer polyacrylate component used in accordance with the invention as pasting resin may be produced from polyols, dicarboxylic acids and diols. Polycondensation is effected according to conventional processes familiar to one skilled in the art, for example in the presence of conventional esterification catalysts and at elevated temperatures of, eg, 180 to 230 °C in a melt.

Examples of the polyol are those with more than two OH groups, such as aliphatic triols and tetrols with 2 to 6 carbon atoms, such as trimethylolethane, trimethylolpropane, glycerine, 1,2,4-butanetriol, 1,2,6-hexanetriol and pentaerythritol.

Examples of the dicarboxylic acids are aliphatic saturated and unsaturated dicarboxylic acids such as maleic acid, fumaric acid, succinic acid, adipic acid, azelaic acid, sebacic acid; cycloaliphatic saturated and unsaturated dicarboxylic acids and aromatic dicarboxylic acids, such as phthalic acid, isophthalic acid, endomethylenetetrahydrophthalic acid, endoethylenetetrahydrophthalic acid and cyclohexane dicarboxylic acid (1.2, 1.3 and 1.4), itaconic acid, muconic acid and camphoric acid, or optionally the possible anhydrides thereof.

Examples of useable diols are aliphatic diols such as ethylene glycol, propylene glycol (1.3 and 1.2), butanediol, hexanediol

(1.6), neopentyl glycol; polyether glycols of ethylene and of propylene with up to 6 monomer structural units, such as diethylene glycol, triethylene glycol, tetraethylene glycol and hexaethylene glycol; and cycloaliphatic diols such as 1.3-dimethylolcyclohexane and 1.4-dimethylolcyclohexane.

In the polyester oligomer or the solution thereof, in a monoalcohol for example, a hydroxyfunctional (meth)acrylate ester, a monoethylenically unsaturated acid and optionally a (meth)acrylic acid ester without hydroxy functions, either on their own or in a mixture, are subjected to radical polymerisation in the presence of a radical initiator. Examples of radical initiators are:

dialkyl peroxides such as di-tert.-butyl peroxide, di-cumyl peroxide; diacyl peroxides such as di-benzoyl peroxide, di-lauroyl peroxide; hydroperoxides such as cumene hydroperoxide, tert.-butyl hydroperoxide; peresters such as tert.-butylperbenzoate, tert.-butylperpivalate, tert.-butyl-per-3,5,5-trimethylhexanoate, tert.butyl-per-2-ethylhexanoate; peroxydicarbonates such as di-2-ethylhexyl-peroxydicarbonate, dicyclohexyl-peroxydicarbonate; perketals such as 1,1-bis-(tert.-butylperoxy)3,5,5-trimethylcyclohexane, 1,1-bis(tert.-butylperoxy)-cyclohexane; ketone peroxides such as cyclohexanone peroxide, methylisobutylketone peroxide and azo compounds such as 2,2'-azo-bis(2,4-dimethylvaleronitrile), 2,2'-azo-bis(2-methylbutyronitrile), 1,1'-azo-biscyclohexanecarbonitrile, azo-bis-isobutyronitrile.

The radical initiators are generally added in a quantity of 0.1 to 4 wt% relative to the weighed sample of monomer.

Examples of the useable hydroxyfunctional (meth)acrylic esters a) are (meth)acrylic esters of ethylene glycol, propylene glycol (1.2 and 1.3), butanediol (1.4), hexanediol (1.6), as well as polyethylene glycol mono(meth)acrylate with 6 to 8

ethylene glycol units and n-propylene glycol mono(meth)acrylate with 5 to 6 propylene glycol units. Preferred examples are hydroxyethylacrylate-caprolactone adducts, butanediol(1.4)mono(meth)acrylate, polypropylene glycol mono(meth)acrylate and polyethylene glycol mono(meth)acrylate.

Examples of the α,ß-ethylenically unsaturated carboxylic acids b) are acrylic acid or methacrylic acid, as well as maleic acid and fumaric acid and the half-esters thereof with aliphatic alcohols.

Examples of the α,ß-ethylenically unsaturated monomers c) without functional groups are: (meth)acrylic acid esters of alcohols with 1 to 12 carbon atoms in the chain, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, butyl(n-, iso- and tert.-) alcohol, hexyl alcohol, 2-ethylhexyl alcohol and lauryl alcohol, as well as aromatic vinyl compounds such as styrene, vinyltoluene and α-methylstyrene.

Paste resins which are useable according to the invention are obtained in solvent-free or organically dissolved form.

With a view to production of the pigment paste according to the invention the polyester oligomer polyacrylates can also be used after being neutralised with bases. The amines which are customary in the lacquering industry are particularly suitable as bases, whereby use is preferably made of volatile organic amines of low molecular weight, or of ammonia. Neutralisation of the polyester oligomer polyacrylate is optionally effected subject to heating with a view to obtaining a favourable working viscosity, or after addition of water-compatible or water-soluble organic solvents. The base is added in such an amount as to ensure that the pH-value of the neutralised product obtained lies around 7.0 to 10 after dilution with water and is preferably 7.5 to 9.

It is possible for all conventional known pigments to be worked into the pigment pastes according to the invention. The term "pigments" here should be understood to mean all conventional inorganic and/or organic pigments, but also fillers and other dyestuffs.

For the pigment pastes according to the invention use can be made in particular of all conventional inorganic and/or organic colouring pigments, such as carbon black, titanium dioxide, and pigments made from phthalocyanine, perylene or quinacridone. Effect-producing pigments such as metallic pigments or interference pigments may also be added. To these it is in addition possible to add colourless pigments - eg, micronised titanium dioxide or silicon dioxide or dyestuffs with a view to obtaining special optical effects.

With the process according to the invention the ratio of pigment or filler to paste resin is preferably in the range 0.05 to 2.5 : 1 relative to the weight of solids, depending on the type of pigment used.

During or after production it is possible to add to the pigment pastes according to the invention further conventional additives such as dispersing agents, anti-foam agents, wetting agents and anti-settling agents such as pyrogenic silicon dioxide. It is also possible to add to the pigment paste further aids which are customary in lacquering and which are to be supplied to the complete coating agent - eg, levelling agents.

The pasting operation in the process according to the invention may be effected in the customary manner familiar to one skilled in the art, for example by dispersing the pigments in suitable grinding aggregates such as pearl mills, and requires no further explanation.

Pasting is preferably effected in the organic solution of the

polyester oligomer polyacrylate or in the solvent-free form thereof. The mixture consisting of the paste resin, which is optionally dissolved, pigments, fillers and additives is dispersed until the desired fineness of grain of the pigments is obtained. Suitable grain sizes generally have a magnitude of up to about 15 μm, preferably below 10 μm.

Effect-producing pigments, such as metallic or pearlescent pigments, are mixed with or solubilised in polyester oligomer polyacrylate used according to the invention or the organic solution thereof, resulting in the formation of an effect-producing pigment paste.

As a result of this working method the occurrence of foam is largely prevented and a universally useable pigment paste is obtained which is stable in storage and when exposed to frost.

From these pastes optionally containing organic solvents it is possible to produce aqueous pigment pastes by dilution with water after prior neutralisation with bases. Suitable by way of bases are, in particular, the amines which are customary in the lacquering industry, whereby use is preferably made of volatile organic amines of low molecular weight, or of ammonia.

The pigment pastes produced according to the invention can be used for the production of water-dilutable and solvent-based pigmented coating agents. For this purpose they are, in each case, converted into a suitable aqueous or non-aqueous form. They are suitable in particular for the pigmentation of basecoat and topcoat lacquers.

The coating agents may be of the physically drying or the chemically crosslinking type. The pigmented coating agents may be of the one-component or the multi-component type. Examples are conventional or water-dilutable basecoat lacquers, conventional or water-dilutable oxidatively drying

synthetic resin lacquers, conventional or water-dilutable one-component or multi-component topcoat lacquers of the chemically crosslinking type.

The chemically crosslinking topcoat lacquers are preferably based on those crosslinking mechanisms which proceed by virtue of reactions of hydroxyl groups, such as the formation of urethane with optionally blocked isocyanate groups of conventional polyisocyanate crosslinking agents, the formation of ether, eg, by transetherification with alkoxymethyl groups of conventional aminoplastic crosslinking agents, transesterification/transamidisation with conventional transesterification/transamidisation crosslinking agents. But of course the pigment pastes according to the invention can also be used in coating agents which are crosslinkable as a result of other crosslinking reactions.

For the production of pigmented coating agents it is possible to add to the pigment pastes produced according to the invention lacquer binding agents, optionally crosslinking agents, conventional lacquering additives, solvents, in the case of water-dilutable coating agents optionally also neutralising agents and water in a suitable sequence, whereupon thorough homogenisation is effected. The lacquer binding agents are present in organically dissolved form or, in the case of production of water-dilutable pigmented coating agents, optionally also in a form diluted with water. The processes for producing coating agents are familiar to one skilled in the art and are established in accordance with the coating system selected.

The choice of the lacquer binding agents depends on the technological demands which the coating to be produced therewith has to meet. Thus conventional lacquer binding agents - eg, polyesters, acrylate resins or polyurethanes - may be used by way of lacquer binding agents. The crosslinking agents described in the literature may be added.

One or several different binding agents and crosslinking agents may be used. Optionally it is also possible to add further binding agents of the type represented by the paste resins mentioned above by way of lacquer binding agents.

In general the proportion of the polyester oligomer polyacrylate used for production of the pigment pastes according to the invention, said polyester oligomer polyacrylate being contained in the coating agents pigmented with said pigment pastes, amounts to up to 50 wt% relative to the solid resin (sum of paste resin plus binding agent plus, optionally, crosslinking agent). This preferably amounts to less than 30 wt%. Optionally the paste resin used in the pigment paste may also be the sole binding agent in addition to the crosslinking resin, as, for example, in the case of water-dilutable topcoat lacquers. Then the ratio of paste resin to crosslinking agent lies between 60:40 and 90:10 relative to the weight of solids.

In physically drying coating agents or coating agents which crosslink without the incorporation of hydroxyl groups the proportion of solid resin of the paste resin used according to the invention lies below 20 wt%, preferably below 15 wt%.

Attention should be paid to the fact that the pigment pastes produced according to the invention do not have a negative influence on the storage stability of the coating agents formulated therewith. Thus the pigment pastes used according to the invention in the case of two-component polyurethane topcoat lacquers, for example, should not be a constituent of the isocyanate component. Likewise it is favourable to combine the aqueous pigment pastes only with binding agents which are similarly charged. It is favourable to produce non-aqueous coating agents with non-aqueous pigment pastes.

The pigment pastes produced according to the invention can also be used for the tinting of coating agents. For this

purpose they are used in small quantities. Use as tinting paste is possible in all water-dilutable or conventional coating agents, also in fillers for example. The pigment pastes produced according to the invention are characterised by universal applicability - ie, in both water-dilutable and conventional coating agents. They do not require any particular measures to be taken during production, such as the combating of foam problems or the provision of corrosion-resistant production plants. In the water-free form there is no change in their stability in storage or their stability when exposed to frost.

The coating agents produced subject to the use of the pigment pastes produced according to the invention are suitable for the production of pigmented coatings of high optical quality and satisfy today's technological requirements.

The following examples elucidate the invention. Percentage figures relate to weight unless otherwise stated.

Production of a polyester oligomer

Example 1:

336.7 g trimethylolpropane, 366.8 g adipic acid and 297 g hexanediol are esterified with 5 g hypophosphoric acid in a 2-litre three-necked flask equipped with stirrer, separator, thermometer and reflux condenser at 180 °C to 230 °C in a melt so as to yield an acid number of 20.

Subsequently condensation is effected in a vacuum until an acid number < 1.5 is attained.

The product so obtained has a stoving residue of 94.5% (1 h, 150 °C), a viscosity of 3200 mPas (100%), a hydroxyl number of 460 and a colour number of 30 Haze.

Production of polyester oligomer polyacrylates

Example 2:

717 g of the oligoester from Example 1 are submitted with 311 g butoxyethanol in a 4-litre three-necked flask equipped with stirrer, reflux condenser, dropping funnel and thermometer and heated to 140 °C.

Subsequently a mixture consisting of 552 g butanediol monoacrylate, 946 g tert. butyl acrylate, 74 g acrylic acid and 100 g Trigonox C (tert. butylperbenzoate) is added dropwise for 4 hours and further polymerised for 4 hours.

The product had a stoving residue of 84.0% (1 h, 150 °C) according to DIN 53182, a viscosity of 15830 mPas (DIN 53015), an acid number of 38.0 mg KOH/g solids (DIN 53402), an OH-number of 231 mg KOH/1 g solids (DIN 53240) and a colour number of 60 Haze (DIN 53409).

Production of pigment pastes

Example 3:

81.6 parts of the paste resin solution from Example 2 were diluted under the dissolver with 2 parts hexylene glycol and 10.4 parts butoxyethanol. Subsequently 6 parts pyrogenic silica (Aerosil R 972, manufactured by Degussa) were stirred in uniformly and ground in a pearl mill at 60 °C to a fineness of grain of 10 µm.

Example 4:

Under the dissolver 65 parts of the paste resin solution from Example 2 were added to 10 parts of the paste from Example 3 and 10 parts of a solvent mixture consisting of butoxyethanol, hexylene glycol and ethanol in a weight ratio of 8:2:2, 5

parts carbon black were simultaneously stirred in and diluted with an additional 10 parts of the aforementioned solvent mixture. Subsequently thorough grinding was effected in a pearl mill at 60 °C to a fineness of grain of < 10 µm.

Example 5:

Under the dissolver 23 parts of the paste resin solution from Example 2 were added to 10 parts of the pigment paste from Example 3 and 7 parts of the solvent mixture from Example 4. Subsequently 60 parts of titanium dioxide were stirred in uniformly and then ground thoroughly in a pearl mill at 60 °C to a fineness of grain of 10-12 µm.

Example 6:

Under the dissolver 60 parts of the paste resin solution from Example 2 were added to 10 parts of the pigment paste from Example 3 and 20 parts of the solvent mixture from Example 4. Subsequently 10 parts of phthalocyanine blue (Heliogenblau L 6975 F, manufactured by BASF) were stirred in uniformly and then ground thoroughly in a pearl mill at 60 °C to a fineness of grain of < 10 µm.

Example 7:

Under the dissolver 10 parts of the paste resin solution from Example 2 were added to 10 parts of the solvent mixture from Example 4. Subsequently 33 parts of a commercial aluminium paste (65% in test benzine/Solvesso 100, Alupaste R 507 ES, manufactured by Eckert) were stirred in and diluted with 47 parts of the aforementioned solvent mixture. Stirring was effected for 15 minutes at 20 °C.

Production of pigmented lacquers

Example 8: (solvent-based 1-component topcoat lacquer)

In the table below the stated quantities of a 70% solution of a medium-oily, non-drying alkyd resin were submitted with a proportion of phthalic acid of 32% dissolved in Solvesso 100 (I), a 55% isobutanolic solution of an melamine formaldehyde resin (II) etherified with isobutanol and the pigment paste was then added under the dissolver in accordance with the table below. After uniform intermixing 0.4 parts of a commercial levelling agent based on organosiloxane and 0.8 parts of a 1% xylolic solution of a phenylmethylsiloxane were added in each case and diluted with 11 parts of a solvent mixture consisting of 36% of a terpene hydrocarbon, 46% Solvesso 100 and 18% butyl acetate.

Example	Amount I	Amount II	Paste
8 a	25 parts	28 parts	34.8 parts from Ex. 4
8 b	25 parts	21 parts	41.8 parts from Ex. 5
8 c	21 parts	26.5 parts	40.3 parts from Ex. 6

Example 9: (water-dilutable 1-component topcoat lacquer)

25 parts of the paste resin solution from Example 2 were added under the dissolver to 14 parts of the pigment paste from Example 5, 9.5 parts of the pigment paste from Example 6 and 0.4 parts of the pigment paste from Example 4. After homogenisation 20 parts of a solution of 1 part dimethylethanol amine in 10 parts deionised water were slowly added and then carefully diluted with 14.1 parts of a mixture consisting of ethanol, butanol, butoxyethanol and deionised water in a ratio of 1:1:2:25. After homogenisation 17 parts of an 85% isobutanolic solution of a highly aminofunctional

melamine formaldehyde resin etherified with methanol were stirred in.

Example 10: (solvent-based 2-component topcoat lacquer)

70 parts of a 55% solution of an acrylate resin with an acid number of 7 and a hydroxyl number of 140 mg KOH/g in a mixture consisting of xylene, butyl acetate and Solvesso 100 in a ratio of 20:16:9 were added under the dissolver to 11.9 parts of the pigment paste from Example 6, 0.5 parts of the pigment paste from Example 4 and 17.6 parts of the pigment paste from Example 5. Prior to application there were added to 100 parts of this mixture 50 parts of a 41% solution of an aliphatic polyisocyanate (Desmodur N 3390, manufactured by Bayer) in a mixture consisting of methoxypropyl acetate, Solvesso 100, butyl acetate and butyl glycol acetate in a ratio of 50:5:30:15 by way of crosslinking agent.

Example 11: (solvent-based metallic basecoat lacquer)

20 parts of a 55% solution of a commercial copolymer of ethylene and acrylic acid with an acid number of 40 mg KOH/g in a mixture consisting of butyl acetate and xylene in a ratio of 1:1 were added under the dissolver to 25 parts of a 25% solution of cellulose acetobutyrate (acetyl content 15%, butyryl content 37%, hydroxyl content 0.8%) in a mixture consisting of butyl acetate and butanol in a ratio of 2:1, 9.5 parts of a 65% solution of a branched polyester with an acid number of 20 and a hydroxyl number of 80 mg KOH/g and a molecular weight (M_w) of 2000 in xylene, 4.5 parts of a 55% butanolic solution of a melamine formaldehyde resin etherified with butanol and 4 parts of a carbamic acid resin based on butyl urethane and formaldehyde. Then 15 parts of the effect-producing pigment paste from Example 7 were stirred in homogeneously and diluted with 20 parts butyl acetate.

The pigment pastes contained in Examples 3 to 7 are stable in storage. They exhibit no tendency towards sedimentation and can be processed into coating agents even after storage. They can also be stored at -5 °C without becoming unusable.

The coating agents of Examples 8 to 11 exhibit good technical lacquering properties. They form coating agents which are stable in storage.

Herberts GmbH

Claims:

1. Pigment paste containing a paste resin based on a polyester oligomer polyacrylate which is obtainable by radical polymerisation of

   A) 80 - 50 wt% of
   a) one or several hydroxyfunctional acrylic acid esters and/or methacrylic acid esters and
   b) one or several monofunctional ethylenically unsaturated acids, and, optionally,
   c) one or several alpha,beta-ethylenically unsaturated monomers differing from a) and b) and without functional groups in

   B) 20 - 50 wt% of one or several hydroxyfunctional polyester oligomers with a calculated molecular weight of 200 - 1000, a hydroxyl number of 280 - 600 and an acid number of 0 - 1.5, obtainable by polycondensation of one or several diols, polyols and dicarboxylic acids and derivatives thereof,

   whereby the monomers a), b) and c) are used in such quantities as to ensure that the polyester oligomer polyacrylate obtained has a hydroxyl number of 150 - 390 and an acid number of 16 - 40,

   and, made into a paste therein or blended therewith, one or several pigments and/or fillers in a ratio of pigment or filler to paste resin of 0.05 to 2.5 : 1 relative in each case to the weight of solids.

2. Process for the production of a pigment paste by pasting or blending one or several pigments and/or fillers in a paste resin, characterised in that a paste resin based on a polyester oligomer polyacrylate is used which is obtainable by radical polymerisation of

A) 80 - 50 wt% of

a) one or several hydroxyfunctional acrylic acid esters and/or methacrylic acid esters and

b) one or several monofunctional ethylenically unsaturated acids, and, optionally,

c) one or several alpha,beta-ethylenically unsaturated monomers differing from a) and b) and without functional groups in

B) 20 - 50 wt% of one or several hydroxyfunctional polyester oligomers with a calculated molecular weight of 200 - 1000, a hydroxyl number of 280 - 600 and an acid number of 0 - 1.5, obtainable by polycondensation of one or several diols, polyols and dicarboxylic acids and derivatives thereof,

whereby the monomers a), b) and c) are used in such quantities as to ensure that the polyester oligomer polyacrylate obtained has a hydroxyl number of 150 - 390 and an acid number of 16 - 40,

3. Pigment paste or process according to Claim 1 or 2, characterised in that the radical polymerisation is carried out in the absence of solvents.

4. Pigment paste or process according to Claim 1 or 2, characterised in that the radical polymerisation is carried out in the presence of one or several organic solvents.

5. Pigment paste or process according to one of Claims 1 to 4, characterised in that the pasting or blending is effected in the absence of water.

6. Pigment paste or process according to one of Claims 1 to 5, characterised in that after the pasting or blending the pigment paste is converted into the aqueous phase by neutralisation and dilution with water.

7. Process for the production of coating agents, characterised in that they are pigmented with a pigment paste as defined in one of Claims 1 or 3 to 6.

8. Use of a polyester oligomer polyacrylate, obtainable by radical polymerisation of

A) 80 - 50 wt% of
a) one or several hydroxyfunctional acrylic acid esters and/or methacrylic acid esters and
b) one or several monofunctional ethylenically unsaturated acids, and, optionally,
c) one or several alpha,beta-ethylenically unsaturated monomers differing from a) and b) and without functional groups in

B) 20 - 50 wt% of one or several hydroxyfunctional polyester oligomers with a calculated molecular weight of 200 - 1000, a hydroxyl number of 280 - 600 and an acid number of 0 - 1.5, obtainable by polycondensation of one or several diols, polyols and dicarboxylic acids and derivatives thereof,

whereby the monomers a), b) and c) are used in such quantities as to ensure that the polyester oligomer polyacrylate obtained has a hydroxyl number of 150 - 390 and an acid number of 16 - 40,

by way of paste resin for the pasting of opaque pigments and/or fillers or for blending with effect-producing pigments.

9. Use of the pigment pastes as defined in Claims 1 or 3 to 6 for the pigmentation of aqueous and non-aqueous coating agents.

10. Use of the coating agents obtained according to the process of Claim 7 for the production of lacquer coatings.

COULBOKA

\\server\name

PSCRIPT Page Separator

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08F 002/38, C07C 327/26

A1

(11) International Publication Number: WO 92/13903

(43) International Publication Date: 20 August 1992 (20.08.92)

(21) International Application Number: PCT/AU92/00029

(22) International Filing Date: 31 January 1992 (31.01.92)

(30) Priority data:
PK 4465 6 February 1991 (06.02.91) AU

(71) Applicant *(for all designated States except US)*: COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU/AU]; Limestone Avenue, Campbell, ACT 2601 (AU).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : MEIJS, Gordon, Francis [AU/AU]; 3 Henty Street, Murrumbeena, VIC 3163 (AU). RIZZARDO, Ezio [AU/AU]; 26 Alex Avenue, Wheelers Hill, VIC 3150 (AU).

(74) Agents: CORBETT, Terence, Guy et al.; Davies Collison Cave, 1 Little Collins Street, Melbourne, VIC 3000 (AU).

(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent), US.

Published
With international search report.

(54) Title: POLYMERISATION REGULATION

$$R^1 - \overset{\overset{S}{\|}}{C} - Z - R^2 \qquad (I)$$

(57) Abstract

A process for the production of low molecular weight polymers by free radical polymerisation of one or more monomers in the presence of a chain transfer agent, characterized in that the chain transfer agent comprises one or more compounds of general formula (I), wherein R^1 is a hydrogen atom, an alkyl group, or a group capable of activating the vinylic carbon towards free radical addition; R^2 represents an optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, or optionally substituted satured, unsatured or aromatic carbocyclic or heterocyclic ring; and Z represents an oxygen, sulphur, phosphorus, or nitrogen atom bound to another atom or group of atoms in order to satisfy its valency.

POLYMERISATION REGULATION

The invention relates to processes for radical-initiated polymerisation of unsaturated species and for the regulation of molecular weight and end-group functionality of the polymeric products produced from such processes. Polymers of limited molecular weights, or oligomers, are useful as precursors in the manufacture of other polymeric materials and as additives or components of formulations for plastics, elastomerics, and surface coating compositions, as well as being useful in their own right in many applications. For example, low molecular weight polymers are often required for ease of processing. End-functional polymers are important as building-blocks for advanced copolymers. If of sufficiently low molecular weight, end functional polymers often display useful surface active or compatibilising properties.

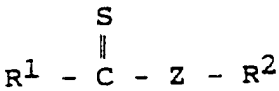
In conventional polymerisation practice, the manufacture of low molecular weight polymers requires the use of an initiator and a chain transfer agent. The initiator acts as a free radical source, whereas the chain transfer agent or regulator controls the molecular weight of the polymer molecule by reacting with the propagating polymer radical to terminate its growth. The chain transfer agent then causes the initiation of a new polymer chain thus transferring the growth process from one discrete polymer molecule to another discrete polymer molecule. At least a part of the chain transfer agent is incorporated into the polymer molecule and is thereby consumed in the process.

The chain transfer agents most commonly used are alkanethiols which possess an objectionable odour, lead to a wide distribution of molecular weights in batch polymerisations with certain monomers, do not allow the production of di-end functional polymers and have limitations as to the types of functional groups that can be installed at the end of the polymer chain. There is also little scope with thiols for the chain transfer constant to be optimised for a particular polymerisation. In many polymerisations with thiols, the chain transfer constant, a measure of the effectiveness of the polymerisation regulator, departs significantly

from the ideal of 1.0 that is the optimum for batch polymerisations at moderate to high conversions. The desirability of chain transfer constants close to 1.0 is reviewed by an article by T. Corner in *Advances in Polymer Science*, volume 62, p. 95 (1985). International Patent Application PCT/AU87/00412 and Australian Provisional Patent Application PJ7146/89 disclose novel polymerisation processes employing regulators that help overcome many of the disadvantages of thiols, particularly in relation to chain transfer constant and, in part, provide polymerisation processes that give alternative end groups. They also allow incorporation of a wider variety of useful functional groups at the ends of polymer chains.

The present invention seeks to overcome the disadvantages of polymerisations regulated with thiols by using alternative polymerisation regulators. These regulators have good stability and shelf life while maintaining many of the advantages over thiols. In the majority of cases, the materials that are part of the present process present a different range of chain transfer activities, allowing more opportunity for an optimal process to be selected for a given polymerisation system of monomers and polymerisation conditions. The chain transfer constant that a given regulator possesses is an important consideration in selecting the optimum process for producing low molecular weight polymers.

The present invention provides a process for the production of low molecular weight polymers by free radical polymerisation, which process is characterised by the addition to the polymerisation system of a compound of the general formula I



(I)

wherein

R^1 is a hydrogen atom, an alkyl group, or preferably, a group capable of activating the vinylic carbon towards free radical addition;

R^2 represents an optionally substituted alkyl, optionally substituted alkenyl,

optionally substituted alkynyl, or optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring; and

Z represents an oxygen, sulphur, phosphorus, or nitrogen atom bound to another atom or group of atoms in order to satisfy its valency.

Suitable groups for R^1 are optionally substituted phenyl or other optionally substituted aromatic groups, alkoxycarbonyl or aryloxycarbonyl (-COOR), carboxy (-COOH), acyloxy ($-O_2CR$), carbamoyl ($-CONR_2$), and cyano (-CN), where R is an alkyl or aryl group.

Optional substituents for R^1 and/or R^2 in formula I may comprise either reactive or non-reactive groups. "Reactive substituent groups" are groups which do not take part in the actual lowering of the molecular weight but are installed at the ends of the polymer chains and may be capable of subsequent chemical reaction. The low molecular weight polymer containing such a reactive group or groups is thereby able to undergo further chemical transformation, such as being joined with another polymer chain. Suitable reactive substituents include hydroxy (-OH), amino ($-NH_2$), halogen, allyl, cyano, epoxy, and carboxylic acid and its derivatives, such as ester groups (-COOAlkyl). "Non-reactive substituent groups" may be any groups which are not deleterious to the polymerisation reaction or product, for example, alkoxy (-OAlkyl) or alkyl groups.

Substituted rings may have their reactive substituent groups directly attached to the ring or indirectly attached by means of a methylene group or other side chain.

Alkyl groups referred to in this specification may contain from 1 to 32 carbon atoms. Alkenyl and alkynyl groups may contain from 2 to 32 carbon atoms. Saturated, unsaturated, or aromatic carbocyclic or heterocyclic rings may contain from 3 to 14 atoms.

The process of this invention may be adopted by the users of conventional

processes using thiols with little change to reaction conditions other than the substitution of the appropriate quantity of a compound of general formula I for the thiol. The proportion of the compound of general formula I used may be in the range of 0.01 to 30 mole percent based on total monomer, with a preferred range 0.1 to 5 mole percent. The process may be operated at any of the reaction conditions appropriate to free radical polymerisation, i.e. temperatures from -100 °C to 400 °C and pressures from below atmospheric to 3000 atmospheres. Bulk, solution, emulsion, suspension or other conventional polymerisation modes may be used. Any unsaturated monomers susceptible to free radical polymerisation may be used although it should be noted that the chain transfer constant will vary with the monomer used. Suitable unsaturated monomers include acrylic esters, methacrylic esters, acrylonitrile, vinyl halides, vinyl esters, vinyl aromatics, unsaturated or poly unsaturated hydrocarbons, or mixtures of these. For example, the process is applicable to the manufacture of synthetic rubbers, and other polymer formulations where reduced molecular weight aids processing and improves properties. The process can also be used to produce low molecular weight polymers and oligomers for a variety of applications such as high-solids surface coatings, paints, and adhesives.

Compounds of general formula I are readily prepared and, unlike the lower molecular weight thiols, they do not possess an objectionable odour. The compounds used in the process of this invention display an unexpected high activity in controlling molecular weight in polymerisation reactions and have chain transfer constants that may be superior to those of thiols, particularly with styrene and acrylates. Their activity is such that their chain transfer constants can approach the optimum of 1.0 for batch polymerisations and this activity is not as highly dependent as that of thiols on the structure of the propagating radical.

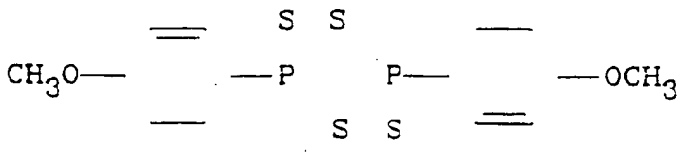
A feature of the process of this invention is that, unlike processes described in many of the examples of International Patent Application PCT/AU87/00412, it produces polymer chains that do not contain terminal unsaturation. In addition, those chain transfer agents described in International Patent Application

PCT/AU87/00412 that specifically do not introduce terminal unsaturation (for example, α-benzyloxystyrene and derivatives) have less satisfactory chain transfer constants and lower shelf life than the compounds of formula I.

An additional, unique feature of the process is that the resulting polymers can be hydrolysed to give a terminal thiol group. Such hydrolysis cleaves off the residue of the chain transfer agent containing R^1 and therefore there is no need for R^1 to contain a functional substituent for the production of thiol terminated polymers. If R^2, however, contains a functional substituent, a di-end functional polymer will be the product of the process (after the hydrolysis step) and one of the end groups will be a thiol group. Thiol terminated polymers have application as odour-free polymeric chain transfer agents and as building blocks for the preparation of block and graft copolymers.

The end functional polymers produced by any of the aspects of the process described above can be converted into polymers with different end functionality by chemical reaction as is well known in the art. For example, hydroxy terminated polymers can be converted into macromonomers by reaction with methacryloyl chloride. These macromonomers are useful materials for the preparation of graft copolymers by free radical copolymerisation.

The materials of formula I that are employed in the process of this invention may be prepared by reaction of the corresponding *O*-ester with Lawesson's reagent or by treatment of alcohols or alkoxides with thiobenzoyl chloride or the sodium salt of (thiobenzylthio)acetic acid. The reaction of iminoesters with hydrogen sulfide has also been reported to give thionoesters.



Lawesson's Reagent

The following illustrates some of the methods used to prepare examples of the compounds used in the process.

Benzyl thionobenzoate:

By method A [Lawesson's reagent]. Benzyl benzoate (2.1 g) was heated at 140 °C for 24 h with Lawesson's Reagent (4.9 g) in anhydrous xylene (10 ml). After removal of the solvent and subjection of the mixture to chromatography on silica gel and recrystallization from pentane at low temperature, benzyl thionobenzoate was obtained in 67% yield. ^{1}H NMR ($CDCl_3$): δ = 5.64 (s, 2H), 7.3-8.2 (m, 10H).

By method B [Thionobenzoyl chloride route]. Thionyl chloride (71 g) was added dropwise to a solution of dithiobenzoic acid (47 g) in anhydrous ether (44 ml). After 7 h of stirring at ambient temperature, the ether and excess thionyl chloride were removed under reduced pressure. The residue was then distilled twice to afford the thioacid chloride (61%): b.p. 54-64 °C [0.01 mmHg]. Triethylamine (2.03 g) was added in one portion to a solution of the thioacid chloride (3.13 g) and benzyl alcohol (2.16 g) in dry acetone (40 ml) under nitrogen with vigorous stirring. The stirring was continued for 15 h at ambient temperature. The mixture was then poured into water and extracted with ether. The extracts were washed and dried (MgSO4) and the residue was subjected to chromatography on silica gel (eluent: hexane) to give a viscous yellow oil (3.0 g) which was crystallised from pentane to afford benzyl thionobenzoate (2.4 g, 53%): m.p. 39-40 °C.

By method C [(Thiobenzylthio)acetic acid route]. Phenylmagnesium bromide was prepared by adding bromobenzene (20 g) in ether (100 ml) dropwise under nitrogen and reflux to a stirred mixture of magnesium turnings (3.2 g) in anhydrous ether (50 ml). After 30 minutes boiling under reflux, the mixture was cooled in ice and carbon disulfide (12 ml) was added dropwise. The mixture was allowed to warm gradually to 20 °C and stirred for a further 15 h. After this period, ice (130 g) was cautiously added, and the organic layer was separated. The sodium salt of chloroacetic acid (12 g) was added to the aqueous phase and the mixture was allowed to stand for 24 h. After this period, it was brought to pH

1 with hydrochloric acid and extracted with ether. The ether extracts were washed with water (x 3), dried ($CaCl_2$), and the solvent was removed to afford a residue that was recrystallised from benzene to give the acid derivative (7.9 g): m.p. 125-126 °C). A portion (1.06 g) was dissolved in dry tetrahydrofuran (125 ml) and sodium hydride (0.48 g) was then added. After the effervescence had ceased, imidazole (0.68 g) was added and the mixture was refluxed for 5 minutes. Benzyl alcohol was then added and the mixture was refluxed for a further 5 min. It was then cooled, poured into water, and extracted with ether. The extracts were washed three times with water, dried and the solvent was removed to give benzyl thionobenzoate (0.72 g), which was further purified by flash chromatography on silica gel (eluent: b.p. 40-60 °C petroleum spirit) and recrystallization from pentane. Yield: 4 g. m.p. 38-39 °C.

(4-Methoxycarbonylbenzyl) thionobenzoate: Method C was used to prepare this compound in low yield (ca. 5% overall) from bromobenzene and methyl (4-hydroxymethyl)benzoate. The thionoester was recrystallised from dichloromethane/hexane: m.p. 90-91 °C. ^1H NMR ($CDCl_3$): δ = 3.92 (s, 3H), 5.74 (s, 2H), 7.2-7.7 (m, SH), 7.9-8.3 (m, 4H). MS (CH^4): m/z 287 (MH^+, 25%),149 (32%).

Benzyl 4-methoxythionobenzoate: This compound was prepared from 4-bromoanisole and benzyl alcohol in 5% overall yield by *Method C*. It was recrystallised from dichloromethane/hexane: m.p. 68-69 °C. ^1H NMR ($CDCl_3$): δ = 3.67 (s, 3H), 5.60 (s, 2H), 6.73 (d, J = 9 Hz, 2H), 7.1-7.6 (m, 5H), 8.13 (d, J = 9 Hz, 2H). MS (CH^4): m/z 259 (MH^+, 10%),135 (100%), 107 (10%), 91 (45%).

(4-Methoxycarbonylbenzyl) 4-methoxythionobenzoate: Method C was used to prepare this compound in 11% overall yield from 4-bromoanisole and methyl (4-hydroxymethyl)benzoate. The crude product was subjected to flash chromatography (eluent: dichloromethane) and recrystallised from dichloromethane/hexane: m.p. 83-85 °C. ^1H NMR ($CDCl_3$): δ = 3.83 (s, 3H), 3.93 (s, 3H), 5.75 (s, 2H), 6.83 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.9-8.3

(m, 4H). MS (CH^4): m/z 317 (MH^+, 3%), 149 (18%), 135 (100%). Accurate mass m/z 317.0836. $C_{17}H_{17}O_4S$ requires m/z 317.0847.

(4-Ethoxycarbonylbenzyl) 4-methoxythionobenzoate: This compound was prepared from 4-bromoanisole and ethyl (4-hydroxymethyl)benzoate by *Method C*. The overall yield was 18% and recrystallization from dichloromethane/hexane was used for purification. m.p. 75-77 °C. ^1H NMR ($CDCl_3$): δ = 1.40 (t, J = 7 Hz, 3H), 3.83 (s, 3H), 4.37 (q, J = 7 Hz, 2H), 5.73 (s, 2H), 6.80 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 8.0-8.4 (m, 4H). MS (CH^4): m/z 331 (MH^+, 40%),163 (40%),135 (100%).

4-(Hydroxymethyl)benzyl thionobenzoate: This compound was prepared using *Method B* in 26% yield from thiobenzoyl chloride and 1,4-benzenedimethanol. After recrystallization from hexane, yellow needles of the thionoester were obtained. m.p. 80-80.5 °C. ^1H NMR ($CDCl_3$): δ = 1.67 (s, 1H), 4.68 (s, 2H), 5.68 (s, 2H), 7.40 (m, 7H), 8.17 (d, J = 6 Hz, 2H). MS (EI): m/z 257 (M^+-1, 12%), 241 (90%), 121 (100%). Accurate mass m/z 258.0732. $C_{15}H_{14}O_2S$ requires m/z 258.0714.

The following non-limiting examples illustrate the invention.

EXAMPLE 1

Preparation of Low Molecular Weight Polystyrene with Benzyl Thionobenzoate

Azobisisobutyronitrile (35 mg) was dissolved in freshly distilled styrene (25 ml). Aliquots (5.0 ml) were removed and added to ampoules containing the amount of benzyl thionobenzoate shown below in Table 1. The mixtures were polymerised at 60 °C for 1 h in the absence of oxygen. The contents of the ampoule were then poured into methanol and the precipitated polymer was collected and dried *in vacuo* overnight. A small portion was examined by gel permeation chromatography (GPC) using a Waters Instrument connected to six μ-Styragel columns (10^6, 10^5, 10^4, 10^3, 500, and 100 Å pore size). Tetrahydrofuran was used

as eluent at a flow rate of 1 ml/min and the system was calibrated using narrow distribution polystyrene standards (Waters). The results appear in Table 1.

Table 1

Amount of benzyl thionobenzoate added	Conversion %	$\bar{M}_n$
81 mg	2.7	11400
41 mg	2.9	20800
21 mg	3.0	37600
0 mg	3.2	124000

The chain transfer constant (C_x), calculated from these data, was 1.0 which compares favourably with that from n-butanethiol (C_x = 21-25). These results show that the compound is an efficient chain transfer agent and that the process produces polymers of low molecular weight in a controlled manner.

EXAMPLE 2

Preparation of Low Molecular Weight Poly(methyl acrylate) with Benzyl Thionobenzoate

Azobisisobutyronitrile (9 mg) was dissolved in freshly distilled methyl acrylate (25 ml). Aliquots (2.0 ml) were removed and added to ampoules containing thiophen-free benzene (8 ml) and the amount of benzyl thionobenzoate shown below in Table 2. The mixtures were polymerised at 60 °C for 1 h in the absence of oxygen. The volatiles were then removed and the polymers were dried *in vacuo* to constant weight and then examined as before. The results appear in Table 2.

Table 2

Amount of benzyl thionobenzoate added	Conversion %	$\bar{M}_n$ *
50 mg	3.8	9020
26 mg	6.0	17700
12 mg	9.2	35600
0 mg	16	473000

* Polystyrene-equivalent number average molecular weight, obtained by GPC.

The chain transfer constant (C_x), calculated from these data, was 1.2, which compares favourably with that from n-butanethiol (C_x = 1.7).

EXAMPLE 3

Preparation of Low Molecular Weight Poly(vinyl acetate) with Benzyl Thionobenzoate

Azobisisobutyronitrile (16 mg) was dissolved in freshly distilled vinyl acetate (100 ml). Aliquots (10.0 ml) were removed and added to ampoules containing the amount of benzyl thionobenzoate shown below in Table 3. The mixtures were polymerised at 60 °C for 1 h in the absence of oxygen. The volatiles were then removed and the polymers were dried *in vacuo* to constant weight and then examined as before. The results appear in Table 3.

Table 3

Amount of benzyl thionobenzoate added	$\bar{M}_n$ *
2.2 mg	1900
0	253000

* Polystyrene-equivalent number average molecular weight, obtained by GPC.

The chain transfer constant (C_x), calculated from these data, was >20. These results show that the compound acts as a very active regulator in polymerisation of vinyl acetate.

EXAMPLE 4

Preparation of Low Molecular Weight Polystyrene with (4-Methoxycarbonylbenzyl) Thionobenzoate

Samples of polystyrene were prepared on the same scale and in the manner of example 1. The amount of (4-methoxycarbonylbenzyl) thionobenzoate added and the results of the polymerisation are shown in Table 4.

Table 4

Amount of (4-methoxycarbonylbenzyl) thionobenzoate added	$\bar{M}_n$
80 mg	23000
40 mg	41900
20 mg	66300
0 mg	142000

The chain transfer constant (C_x), calculated from these data, was 0.59. A sample of low molecular weight polystyrene ($\bar{M}_n$ = 4570) prepared with (4-methoxycarbonylbenzyl) thionobenzoate was examined by ^{1}H NMR spectroscopy and showed signals at δ = 3.83 indicative of the presence of methyl ester groups. Integration of the spectrum and comparison with the integral of the aromatic styrene signal showed there to be an end group functionality of 0.9-1.0. This experiment shows that the process can be used to prepare end functional polymers.

EXAMPLE 5

Preparation of Low Molecular Weight Poly(methyl acrylate) with (4-Methoxycarbonylbenzyl) Thionobenzoate

Samples of poly(methyl acrylate) were prepared according to the directions given in Example 2, except that (4-methoxycarbonylbenzyl) thionobenzoate was used rather than benzyl thionobenzoate. The amount of (4-methoxycarbonylbenzyl) thionobenzoate added and the results of the polymerisation are shown in Table 5.

Table 5

Amount of (4-methoxycarbonylbenzyl) thionobenzoate added	$\bar{M}_n$ *
50 mg	7700
26 mg	14300
12 mg	28300
0 mg	772000

* Polystyrene-equivalent number average molecular weight, obtained by GPC

The chain transfer constant (C_x), calculated from these data, was 1.4, which compares favourably with that from n-butanethiol (C_x = 1.7).

EXAMPLE 6

Preparation of Low Molecular Weight Polystyrene with Benzyl 4-Methoxy(thionobenzoate)

Samples of polystyrene were prepared on the same scale and in the manner of example 1. The amount of benzyl 4-methoxy(thionobenzoate) added and the results of the polymerisation are shown in Table 6.

Table 6

Amount of benzyl 4-methoxy(thionobenzoate) added	$\bar{M}_n$
80 mg	65100
40 mg	93500
20 mg	113000
0 mg	145000

The chain transfer constant (C_x), calculated from these data, was 0.12.

EXAMPLE 7

Preparation of Low Molecular Weight Poly(methyl acrylate) with Benzyl 4-Methoxy(thionobenzoate)

Samples of poly(methyl acrylate) were prepared according to the directions given in Example 2, except that benzyl 4-methoxy(thionobenzoate) was used rather than benzyl thionobenzoate. The amount of benzyl 4-methoxy(thionobenzoate) added and the results of the polymerisation are shown in Table 7.

Table 7

Amount of benzyl 4-methoxy(thionobenzoate) added	$\bar{M}_n$ *
50 mg	10700
26 mg	18600
13 mg	42600
0 mg	394000

* Polystyrene-equivalent number average molecular weight, obtained by GPC

The chain transfer constant (C_x), calculated from these data, was 1.1, which compares favourably with that from n-butanethiol (C_x = 1.7).

EXAMPLE 8

Preparation of Low Molecular Weight Polystyrene with 4-(Methoxycarbonyl)benzyl 4-Methoxy(thionobenzoate)

Samples of polystyrene were prepared on the same scale and in the manner of example 1. The amount of 4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate) added and the results of the polymerisation are shown in Table 8.

Table 8

Amount of 4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate) added	$\bar{M}_n$
81 mg	48400
40 mg	86000
20 mg	105300
0 mg	150000

The chain transfer constant (C_x), calculated from these data, was 0.25. The total average functionality (methoxy and methoxycarbonyl groups) calculated by ^1H NMR on a sample of polystyrene of $\bar{M}n$ = 13300 (prepared with 4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate) was 2.1, which shows that 4-(methoxycarbonyl)benzyl 4methoxy(thionobenzoate) is efficient in introducing functional groups at the termini of polymer chains and that this type of chain transfer agent can be used to prepare end-functional polymers.

EXAMPLE 9

Preparation of Low Molecular Weight Poly(methyl acrylate) with 4-(Methoxycarbonyl)benzyl 4-Methoxy(thionobenzoate)

Samples of poly(methyl acrylate) were prepared according to the directions given in Example 2, except that 4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate) was used rather than benzyl thionobenzoate. The amount of 4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate) added and the results of the polymerisation are shown in Table 9.

Table 9

Amount of 4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate) added	$\bar{M}_n$ *
50 mg	10700
26 mg	18600
13 mg	42600
0 mg	394000

* Polystyrene-equivalent number average molecular weight, obtained by GPC

The chain transfer constant (C_x), calculated from these data, was 1.1, which compares favourably with that from n-butanethiol (C_x = 1.7).

EXAMPLE 10

Preparation of Low Molecular Weight Polystyrene with 4-(Ethoxycarbonyl)benzyl 4-Methoxy(thionobenzoate)

Samples of polystyrene were prepared on the same scale and in the manner of Example 1. The amount of 4-(ethoxycarbonyl)benzyl 4-methoxy(thionobenzoate) added and the results of the polymerisation are shown in Table 10.

Table 10

Amount of 4-(ethoxycarbonyl)benzyl 4-methoxy(thionobenzoate) added	$\bar{M}_n$
616 mg	13500
0 mg	150000

The presence of ethoxycarbonyl and methoxy end groups in the lower molecular weight sample of polystyrene was shown by signals in the ^1H NMR spectrum at δ = 4.28 and 3.83, respectively.

EXAMPLE 11

Preparation of Low Molecular Weight Polystyrene with 4-(hydroxymethyl)benzyl thionobenzoate

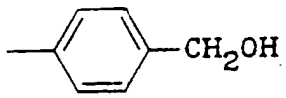
Samples of polystyrene were prepared on the same scale and in the manner of example 1. The amount of 4-(hydroxymethyl)benzyl thionobenzoate added and the results of the polymerisation are shown in Table 11.

Table 11

Amount of 4(hydroxymethyl)benzyl thionobenzoate added	$\bar{M}_n$
81 mg	25600
40 mg	43900
20 mg	59500
0 mg	113000

The chain transfer constant was 0.43. The presence of the end group shown below in a polymer of $\bar{M}n$ = 6810, prepared with 4-(hydroxymethyl)benzyl

thionobenzoate, was confirmed by a broad signal in the ^1H NMR spectrum at δ = 4.4-4.7 (due to the benzyl methylene hydrogens) and an infrared absorption at 3415 cm^{-1}.



End group of polymer prepared with 4-(hydroxymethyl)benzyl thionobenzoate

After treatment with *t*-butyldimethylsilyl chloride and imidazole, this polymer showed signals at δ = 0.08 in the ^1H NMR spectrum due to the methyls of a *t*-butyldimethylsilyl ether group. The formation of this silyl ether further confirms the presence of a hydroxyl end group.

CLAIMS

1. A process for the production of low molecular weight polymers by free radical polymerisation of one or more monomers in the presence of a chain transfer agent, characterised in that the chain transfer agent comprises one or more compounds of the general formula I

(I)

wherein

R^1 is a hydrogen atom, an alkyl group, or a group capable of activating the vinylic carbon towards free radical addition;

R^2 represents an optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, or optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring; and

Z represents an oxygen, sulphur, phosphorus, or nitrogen atom bound to another atom or group of atoms in order to satisfy its valency.

2. A process as claimed in Claim 1, characterised in that R^1 is a substituted phenyl or other optionally substituted aromatic group, or an alkoxycarbonyl or aryloxycarbonyl, carboxy, acyloxy, carbamoyl, or cyano group.

3. A process as claimed in Claim 1 or Claim 2, characterised in that R^1 and/or R^2 in formula I have one or more reactive substituent groups which do not take part in the actual lowering of the molecular weight but are installed at the ends of the polymer chains and may be capable of subsequent chemical reaction, whereby the low molecular weight polymer product containing the reactive group or groups is thereby able to undergo further chemical transformation.

4. A process as claimed in Claim 3, characterised in that the reactive

substituent group is an hydroxy, amino, halogen, allyl, cyano, epoxy, or carboxylic acid group or a derivative of a carboxylic acid group.

5. A process as claimed in any one of the preceding Claims, characterised in that the compound of general formula I is added to present in an amount of from 0.01 to 30 mole percent based on total monomer.

6. A process as claimed in any one of the preceding Claims, characterised in that the monomer is selected from the groups consisting of acrylic esters, methacrylic esters, vinyl esters, vinyl aromatics, unsaturated or poly unsaturated hydrocarbons, or mixtures of any two or more of such monomers.

7. A process as claimed in any one of the preceding Claims, characterised in that the resulting polymer is hydrolysed to give a terminal thiol group.

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)[6]

According to International Patent classification (IPC) or to both National Classification and IPC

Int. Cl.[5] C08F 002/38, C07C 327/26

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	C08F 002/38, C08F 001/80

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

AU: IPC as above; Australian Classification 09.4-33, 09.4-35

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category*	Citation of Document, [11] with indication, where appropriate of the relevant passages [12]	Relevant to Claim No [13]
X	EP,A, 407059 (JAPAN SYNTHETIC RUBBER CO LTD) 9 January 1991 (09.01.91). Refer to page 3, page 6 lines 1-19, page 13 lines 45-55, page 19 table 1 and claim 1	1, 3, 5-7
X	WO,A, 89/10371 (NORSOLOR) 2 November 1989 (02.11.89). Refer to the abstract	1, 3, 5-7
X	US,A, 4054731 (MARUBASHI et al) 18 October 1977 (18.10.77). Refer to column 2 lines 9-48, column 3 line 44-column 4 line 16, column 5 line 43-column 6 line 11, example 1 and claim 1	1, 3, 5-7
X	US,A, 3838140 (MAYER-MADER, BOLDT) 24 September 1974 (24.09.74). Refer to column 1 and column 2, example II and claim 1	1, 3, 5-7

* Special categories of cited documents : [10]

"A" Document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior t the international filing date but later than the priority date claimed

"T" Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
1 May 1992 (01.05.92)	13 May 1992 (13.05.92)
International Searching Authority	Signature of Authorized Officer
AUSTRALIAN PATENT OFFICE	M BREMERS

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers ..., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4a

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.